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Simultaneous determination of 74 kinds of pesticides in Chinese herbal medicine listed in Chinese pharmacopoeia (2015) by GPC-GC-MS/MS

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Overview

A method for quantitative analysis of 74 pesticides in Chinese herbal medicine by GPC-GCMSMS according to the forthcoming Chinese pharmacopoeia (2015) was successfully applied.

Introduction

Chinese herbal medicine has been widely used, but the pesticides residue in herbal medicine is still a serious issue. The 2015 edition of Chinese pharmacopoeia provides an internal standard method based on the QuEChERS pretreatment and the GC-MS/MS system to determine 74 kinds of pesticides in herbal medicine. Instead of the GC-MS/MS system, we apply the GPC-GC-MS/MS system.

Compare with the GC-MS/MS system, the online GPC cleanup technique of the GPC GC-MS/MS system can purify the sample to some degree so the matrix interference can be decreased. Meanwhile, the GPC-GC-MS/MS system provides a much larger sample volume which can reach 20 µl, so the detection limit of GPC-GC-MS/MS is much lower than GC-MS/MS.

Methods

Sample Preparation

The crushed herb sample was soaked in 1% acetic acid solvent for 30 minutes. Then the acetonitrile and internal standards were added into the solvent to extract target compounds. After the extraction, dispersive SPE purification by PSA, $MgSO_4$, C18, GCB and silica gel was employed to remove matrix interferences such as cholesterol. Then the obtained extract was concentrated. The final extract was analyzed by GPC-GC-MS/MS system.

GPC-GC-MS/MS Analysis

The GPC system was LC-20A of Shimadzu with a CLNpack EV-200 (2.0 mmi.d. x 150 mm) GPC column of Shodex Co.
The GC-MS/MS system was GCMS-TQ 8040 (Shimadzu).

The GC column was made up of an empty column (5 m x 0.53 mm), a precolumn (InertCap 5MS/NP, 5 m x 0.25 mm x 0.25 µm) and a main column (InertCap 5MS/NP, 25 m x 0.25 mm x 0.25 µm).

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Analytical Conditions

Column temperature	: 82 °C (5 min)_8 °C/min _300 °C (7.75 min)
Carrier pressure	: 120 kPa (0 min)_100 kPa/min_180 kPa (4.4 min) -49.8 kPa/min _120 kPa (33.8 min)
Injection mode	: Splitless
Injector temperature	: 120 °C (5 min)_100 °C/min _250 °C (33.7 min)
Ion source temperature	: 200 °C
Interface temperature	: 300 °C
Aquisition mode	: EI-MRM

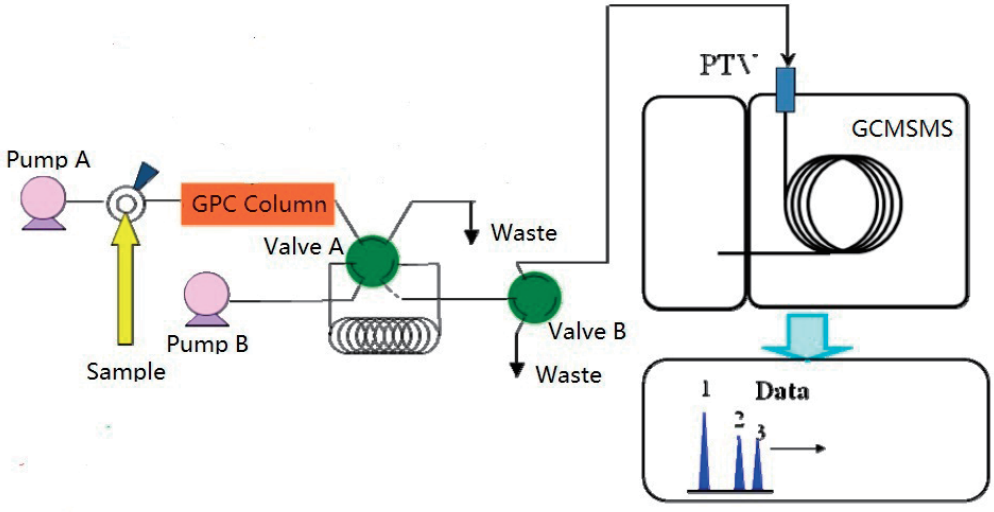

Figure 1 Schematic diagram of the GPC-GC-MS/MS system.

Table 1 GPC time program

Time (min)	Unit	Command	Value
0.1	Option Box vp	Valve A Position	0
0.1	Option Box vp	Valve B Position	0
3.26	Option Box vp	Valve A Position	1
3.86	Controller	Event	1
5.26	Option Box vp	Valve A Position	0
5.46	Option Box vp	Valve B Position	1
8.14	Option Box vp	Degassing Unit State	Operate
8.24	Option Box vp	Degassing Unit State	OFF
8.26	Option Box vp	Valve B Position	0
45	Controller	Stop	

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Results

The online GPC purification was realized by valve switch. The GPC system injected the purified sample into the PTV injector and then the analysis was performed by GC-MS/MS.
All target pesticides are included in the SmartDatabase so the MRM method can be created after one scan mode acquirement to get the retention time of each compound.

Internal standard method was applied to quantitative analysis. Fenthion-d6 was added into the sample as internal standard. The method showed good linearity in the range of 1 ~ 50 ng/mL. The linear correlation coefficient r is bigger than 0.995. With 10 µL sample volume, the LODs of most of the pesticides were less than 0.5ng/mL. The RSD of 6 continuous test was less than 10%. The recoveries of all the pesticides were between 60%~120%.

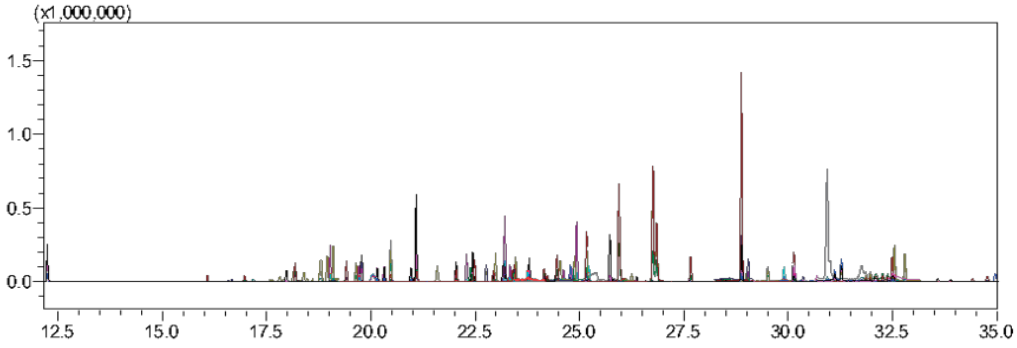

Figure 2 MRM chromatograms of standard mixture (50 ng/mL each)

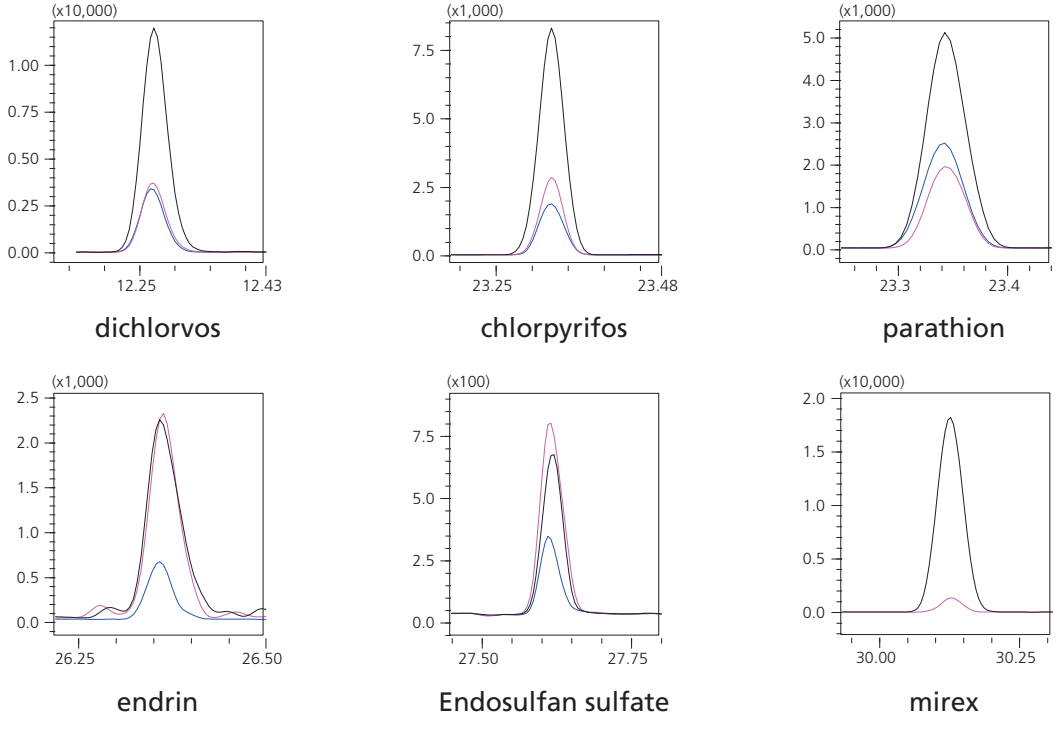

Figure 3 MRM Chromatograms of 6 pesticides (5 ng/mL each)

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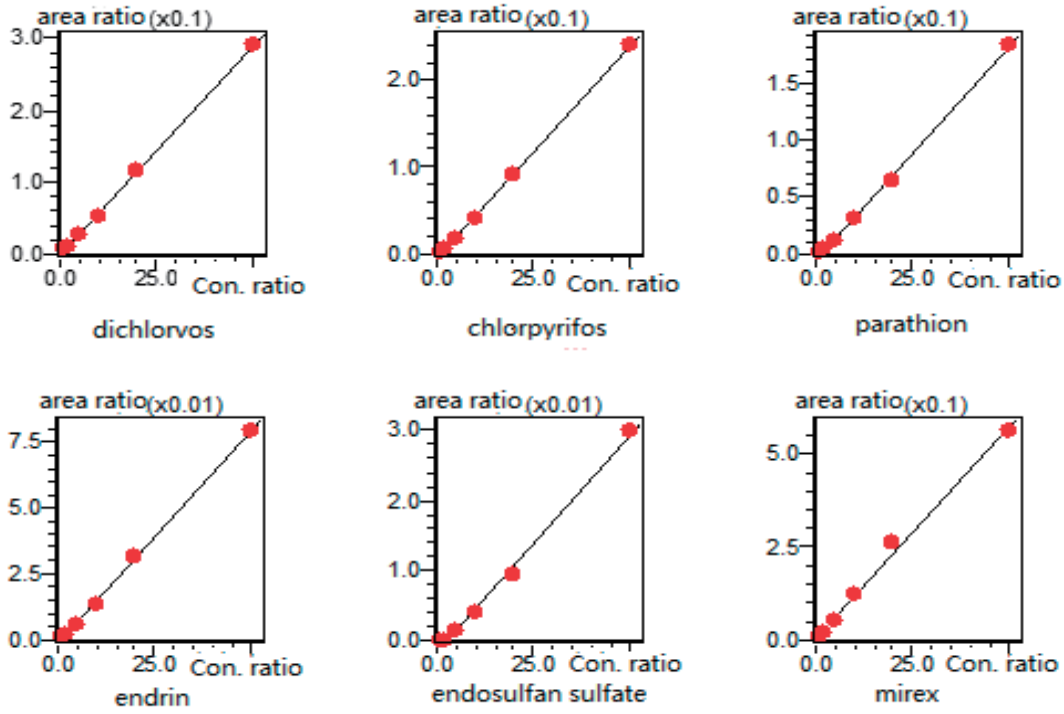

Figure 4 Calibration curve of 6 pesticides

Table 2 Test results of representative compounds

Compound	r	LOD (μg/L)	RSD % (n=6)	Recovery 5 ng/mL
Dichlorvos	0.9996	0.01	3.73	62.11
Diphenylamine	0.9984	0.03	3.88	95.62
Trifluralin	0.9990	0.01	3.72	94.16
alpha-HCH	0.9994	0.10	2.31	102.41
beta-HCH	0.9991	0.01	2.77	104.38
Terbufos	0.9996	0.03	7.75	103.16
Tefluthrin	0.9995	0.01	5.43	103.38
delta-HCH	0.9997	0.07	3.62	89.95
Chlorpyrifos-methyl	0.9995	0.01	2.68	77.29
Vinclozolin	0.9999	0.01	5.60	103.59
Parathion-methyl	0.9999	0.12	6.28	99.75
Heptachlor	0.9999	0.01	3.35	97.18
Fenchlorphos	0.9997	0.03	7.63	102.98
Fenitrothion	0.9993	0.01	4.40	101.31
Aldrin	0.9998	0.01	4.23	78.59
Chlorpyrifos	0.9998	0.01	4.83	84.51

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Conclusions

An online GPC-GC-MS/MS system was successfully applied to analyze 74 pesticides in Chinese herbal medicine. With the purification ability and the large volume sample injection, this system provided good repeatability, low LODs and satisfactory recoveries which can meet the requirements of the Chinese pharmacopoeia (2015).

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